NAKED-EYE DETECTION OF LEAD(II) IN AQUEOUS SOLUTION BY SILICA GEL COATED WITH 1-(2-PYRIDYLAZO)-2-NAPHTHOL

Miss Rungnapa Kongsung

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การตรวจวัดตะกั่ว(II) ในสารละลายน้ำด้วยตาเปล่าโดยใช้ซิลิกาเจล ที่เคลือบด้วย 1-(2-ไพริดิลเอโซ)-2-แนพทอล

นางสาวรุ่งนภา คงสังข์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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Thesis Title	NAKED-EYE DETECTION OF LEAD(II) IN AQUEOUS SOLUTION BY SILICA GEL COATED WITH 1-(2-PYRIDYLAZO)-2-NAPHTHOL
By	Miss Rungnapa Kongsung
Field of Study	Chemistry
Thesis Advisor	Assistant Professsor Wanlapa Aeungmaitrepirom, Ph.D.

Accepted by the Faculty of Science, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

……………………………………...Dean of the Faculty of Science
(Professor Supot Hannongbua, Dr.rer.nat.)

THESIS COMMITTEE

……………………………………...Chairman
(Assistant Professor Warinthorn Chavasiri, Ph.D.)

………………………………………Thesis Advisor
(Assistant Professsor Wanlapa Aeungmaitrepirom, Ph.D.)

………………………………………Examiner
(Assistant Professor Apichat Imyim, Ph.D.)

………………………………………External Examiner
(Withawat Mingvanish, Ph.D.)

รุ่งนภา คงสังข์ : การตรวจวัดตะกั่ว(II) ในสารละลายน้ำด้วยตาเปล่าโดยใช้ซิลิกาเจลที่เคลือบด้วย 1-(2-ไพริดิลเอโซ)-2-แนพทอล (NAKED-EYE DETECTION OF LEAD(II) IN AQUEOUS SOLUTION BY SILICA GEL COATED WITH 1-(2-PYRIDYLAZO)-2-NAPHTHOL) อ. ที่ปรึกษาวิทยานิพนธ์: ผศ.ดร.วัลภา เอื้องไมตรีภิรมย์, 59 หน้า.

เตรียมซิลิกาเจลเคลือบด้วยลิแกนด์มีสี (1-(2-ไพริดิลเอโซ)-2-แนพทอล หรือ PAN) สำหรับตรวจวัดตะกั่ว(II) ด้วยตาเปล่า หาเวลาในการคน ปริมาณซิลิกาเจลและความเข้มข้นของ PAN ที่เหมาะที่สุดในการเคลือบ PAN บนซิลิกาเจล พิสูจน์เอกลักษณ์ผลิตภัณฑ์ Si-PAN โดยดีอาร์-ยูวี-วิซิเบิล สเปกโทรโฟโตเมตรี Si-PAN ที่เคลือบด้วยสารละลาย PAN 0.5 มิลลิโมลาร์ สามารถสกัดตะกั่ว(II) ได้ที่พีเอช 4.5-5.5 ด้วยเปอร์เซ็นต์การสกัด 90 เปอร์เซ็นต์ ภายในเวลา 10 นาที สีของ Si-PAN หลังจากสกัดตะกั่ว(II) แตกต่างจากสี Si-PAN เริ่มต้นอย่างชัดเจนโดยเปลี่ยนจากสีส้มเป็นสีชมพู หาความเข้มข้นของ PAN ที่เหมาะที่สุดในการเคลือบ PAN บนซิลิกาเจลเพื่อให้ได้ความเข้มข้นของตะกั่ว(II) ต่ำที่สุดที่ตรวจวัดได้ด้วยตาเปล่า ผลการทดลองแสดงขีดจำกัดการตรวจวัดตะกั่ว(II) ด้วยตาเปล่า โดยใช้ Si-PAN ที่เคลือบด้วยสารละลาย PAN 0.5 มิลลิโมลาร์ เท่ากับ 0.8 มิลลิกรัมต่อลิตร และพบว่า Si-PAN มีความเลือกจำเพาะต่อตะกั่ว(II) เมื่อเทียบกับไอออนโซเดียม ไอออนโพแทสเซียม ไอออนแมกนีเซียม และไอออนแคลเซียม และไม่พบการเปลี่ยนสีของ Si-PAN เมื่อมีไอออนดังกล่าว ในขณะที่คอปเปอร์(II) เหล็ก(III) และสังกะสี(II) มีผลต่อสีของ Si-PAN หลังการสกัด นอกจากนี้ยังพบว่าใช้ Si-PAN เป็นเซ็นเซอร์ที่มีประสิทธิภาพสำหรับตรวจวัดตะกั่ว(II) ด้วยตาเปล่าได้ 12 สัปดาห์ การตรวจวัดตะกั่ว(II) ในน้ำดื่มด้วยตาเปล่าโดยใช้ Si-PAN ที่เคลือบด้วยสารละลาย PAN 0.5 มิลลิโมลาร์ ทำได้ภายใต้สภาวะที่เหมาะที่สุดในการสกัด

ภาควิชา..........เคมี................. ลายมือชื่อนิสิต...
สาขาวิชา.........เคมี................. ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์ ....
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RUNGNAPA KONGSUNG: NAKED-EYE DETECTION OF LEAD(II) IN AQUEOUS SOLUTION BY SILICA GEL COATED WITH 1-(2-PYRIDYLAZO)-2-NAPHTHOL. ADVISOR: ASST.PROF.WANLAPA AEUNGMAITREPIROM, Ph.D. 59 pp.

Silica gel coated with colorimetric ligand (1-(2-pyridylazo)-2-napthol or PAN) was prepared for Pb(II) naked-eye detection. The stirring time, amount of silica gel and concentration of PAN for coating PAN onto silica gel were optimized. Si-PAN product was characterized by DR-UV-vis spectrophotometry. Si-PAN coated with 5 mM PAN solution was able to extract Pb(II) at pH 4.5-5.5 with 90% extraction within 10 min. After Pb(II) extraction, the color of Si-PAN obviously changed from orange to pink. The concentration of PAN for coating PAN onto silica gel was optimized to detect the lowest concentration of Pb(II) for naked-eye detection. The results showed that the limit of Pb(II) naked-eye detection with Si-PAN coated with 0.5 mM PAN solution was 0.8 mg/L. Si-PAN showed high selectivity towards Pb(II) in comparison with Na^+, K^+, Mg^{2+} and Ca^{2+}. No color change of Si-PAN in the presence of alkali and alkaline earth was observed while Cu(II), Fe(III) and Zn(II) affected to the color of Si-PAN after extraction. Moreover, it was found that Si-PAN was used as an efficient naked-eye sensor for Pb(II) up to 12 weeks. The determination of Pb(II) in drinking water by naked-eye detection using Si-PAN coated with 0.5 mM PAN solution under the optimum extraction conditions was achieved.

Department : Chemistry Student's Signature ....
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R	Absolute reflectance of the sample
pKa	Acid dissociation constant
g	Gram
g/mol	Gram per mole
hr	Hour
L/min	Liter per minute
µL	Micro liter
µM	Micro molar
mA	Mili ampere
mg/L	Miligram per liter
mL	Mili liter
min	Minute
M	Molar
k	Molar absorption coefficient
nm	Nanometer
PAN	1-(2-Pyridylazo)-2-naphthol
rpm	Round per minute
S	Scattering coefficient
SPE	Solid phase extraction
E^0	Standard electrode potential
W	Watt

CHAPTER I

INTRODUCTION SECTION

1.1 Statement of the problem

Lead (Pb) is a non-essential element and an extremely toxic metal. The accumulation of lead causes hematological damage anemia, kidney malfunctioning, brain damage, sore muscles, fatigue, irritation and disturbances in the central nervous system [1]. The maximum acceptable concentration of lead in drinking water is 0.05 mg/L that is regulated by the Pollution Control Department of Thailand. Many people concern about the concentration of lead because of its contamination in drinking water.

Because the contamination of Pb(II) in drinking water is in very low concentration level (lower than the detection limit of some instruments), it cannot be directly measured by spectrometric techniques. The spectrometric techniques such as flame atomic absorption spectrometry (FAAS), inductively-coupled plasma atomic emission spectrometry (ICP-AES) are techniques widely used for determination of various metal ions [2]. Therefore, the sample preparation, i.e. preconcentration is still needed before measured with these instruments. There are many techniques for increasing the concentration of metal ions such as solvent extraction, electro deposition, precipitation, membrane filtration and solid phase extraction (SPE). SPE is an effective technique and mostly used for preconcentration of metal ions [3]. Several sorbents such as activated carbon, silica gel, resin are used in SPE method depending on the objective of the research. Moreover, the surface of the sorbent is often modified for increasing the sensitivity and selectivity for the detection of metal ions [4-5]. The modification of sorbent has been continuously developed and a large number of ligand is modified onto such solid supports. For example, the use of silica gel loaded dithizone for selective extraction of mercury(II) [3] and 4,6-dihydroxy-2-mercaptopyrimidine (DHMP) loaded on activated carbon for preconcentration and determination of copper, nickel, cobalt and lead ions by FAAS [4].

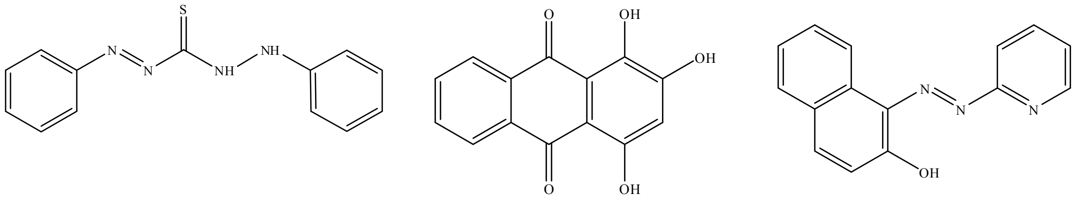
Although SPE has several major advantages but the development of SPE method to detect the metal ions without any instrument is interesting. Naked-eye detection is a colorimetric method which appears or decreases color intensities or changes color because of change in absorption wavelength when the ligand interacts with the target analyte [6]. For example 3-nitro-4-ethylenediamido-nitrobenzene was used as a chemosensor for Cu(II) [7]. The color of the solution changed from yellow to red and a new UV absorption peak at 525 nm was observed when 3-nitro-4-ethylenediamido-nitrobenzene complexed with Cu(II).

Most of researchers studied the naked-eye detection of metal ions in solution. For example, Mitra et al. [8] reported 1-(D-glucopyranosyl-20-deoxy-20-iminomethyl) -2-hydroxynaphthalene as a chemosensor for Fe(III) in aqueous HEPES buffer and Zeng et al. [9] studied a dual functional groups chemosensor of *N*,*N*-bis (pyridine-2-yl-methyl) aniline and quinone units for thiol-containing amino acids and peptides and Zn(II)/Co(II). From a practical point of view, the naked-eye detection of metal ions on solid is considered to provide more convenient and simpler method than the naked-eye detection of metal ions in solution. For example, molybdenum-loaded chelating resin having β-hydroxypropyl-di(β-hydroxyethyl) amino moiety was studied as a sensor for As(V) in an aqueous solution. The resin was separated from the solution by centrifugation and the color of resin was observed by naked-eye [10].

The solid phase extraction can be used for preconcentration of metal ions and the naked-eye detection of metal ions can characterize the kind of metal ion by its characteristic specific color and it can also determine the quantity of metal ion by comparing its color intensity with reference color.

1.2 Objectives of the research

The objectives of this research were (1) to select a suitable ligand from dithizone, purpurin and 1-(2-pyridylazo)-2-naphthol (PAN), illustrated in Fig. 1.1 for coating onto silica gel, (2) to study the optimum conditions for the extraction of Pb(II) from an aqueous solution and (3) to study the potential of the naked-eye detection for Pb(II) by silica gel coated with a suitable ligand.



dithizone **purpirin** **1-(2-pyridylazo)-2-naphthol (PAN)**

Fig. 1.1 Structures of dithaizone, purpurin and 1-(2-pyridylazo)-2-naphthol (PAN).

First, the conditions for coating ligands onto silica gel were optimized. The coating efficiency was evaluated by diffuse reflectance ultraviolet visible (DR-UV-vis) absorption method. The extraction of Pb(II) from an aqueous solution by batch method was studied. The residual concentrations of Pb(II) in aqueous solutions were determined by FAAS and ICP-AES depending on the concentration level of lead. Then, the lowest concentration of Pb(II) which was able to observe the color change by naked-eye was studied under the optimum conditions. The effect of the interfering ions on the metal ions naked-eye detection and the shelf life of silica gel coated with a suitable ligand were also studied. Finally, the determination of Pb(II) in real sample by silica gel coated with a suitable ligand was also carried out.

1.3 Benefit of the research

In this research, the determination of Pb(II) in an aqueous solution by the naked-eye detection using modified silica gel was achieved.

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Chemistry of lead

Lead is a heavy metal with symbol **Pb.** Atomic number of Pb is 82 and atomic weight is 207.2 g/mol. From the periodic table, lead is in group 14 and in period 6. The Pearson's classification of metals and some compounds to hard, soft and borderline Lewis acid is shown in Table 2.1 [11].

Table 2.1 Classification of Lewis acids

Hard	**Soft**
H^+, Li^+, Na^+, K^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Sn^{2+}, Al^{3+}, Se^{3+}, Ga^{3+}, In^{3+}, La^{3+}, Cr^{3+}, Co^{3+}, Fe^{3+}, As^{3+}, Ir^{3+}, Si^{4+}, Ti^{4+}, Zr^{4+},Th^{4+},Pu^{4+}, VO^{2+}, UO_2^{2+}, $(CH_3)_2Sn^{2+}$, $BeMc_2$, BF_3, BCl_3, $B(OR)_3$, $Al(CH_3)_3$, $Ga(CH_3)_3$, $In(CH_3)_3$, RPO_2^+, $ROPO_2^+$, RSO_2^+, $ROSO_2^+$, SO_3, I^{7+}, I^{5+}, Cl^{7+}, R_3C^+, RCO^+, CO_2, NC^+ HX (hydrogen-bonding molecules)	Cu^+, Ag^+, Au^+, Tl^+, Hg^+, Cs^+, Pd^{2+}, Cd^{2+}, Pt^{2+}, Hg^{2+}, CH_3Hg^{2+}, Tl^{3+}, $Tl(CH_3)_3$, RH_3, RS^+, RSe^+, RTe^+, I^+, Br^+, HO^+, RO^+, I_2, Br_2, INC, etc. Trinitrobenzene, etc. Chloranil, quinones, etc. Tetracyanoethylene, etc. O, Cl, Br, I, R_3C, M^0 (metal atoms) Bulk metals
Borderline Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, **Pb^{2+}**, $B(CH_3)_3$, SO_2, NO^+	

In the nature, lead has two oxidation states, Pb(II) and Pb(IV). The electronic structure for Pb(II) is [Xe] $4f^{14}$ $5d^{10}$ $6s^2$ $6p^2$ and for Pb(IV) is [Xe] $4f^{14}$ $5d^{10}$ $6p^2$. In water, lead is easily oxidized to Pb(II) and Pb(IV) compound is easily reduced to

Pb(II) (E^0 value was shown in the equation 2.1 and equation 2.2). Therefore, Pb(II) commonly exists in the environment [12].

$$E^0(Pb(II)/Pb) = -0.13V \qquad (2.1)$$

$$E^0(Pb(IV)/Pb(II)) = 1.69V \qquad (2.2)$$

At the pH of an aqueous solution is below 7 lead is mainly present as Pb^{2+}. With increasing pH, the species such as $PbOH^+$, $Pb(OH)_2$ and $Pb(OH)_3^-$ become dominant over Pb^{2+}. At the high concentration of lead, $Pb_4(OH)_4^{4+}$, $Pb_6(OH)_8^{4+}$ and $Pb(OH)_3^-$ are the major compounds in basic solution and the precipitation of lead-hydroxide compound is observed when the pH of solution is more than 6 [13]. The relative concentration of species of lead depending on pH and total concentration of Pb(II) are illustrated Fig. 2.1 and Fig. 2.2.

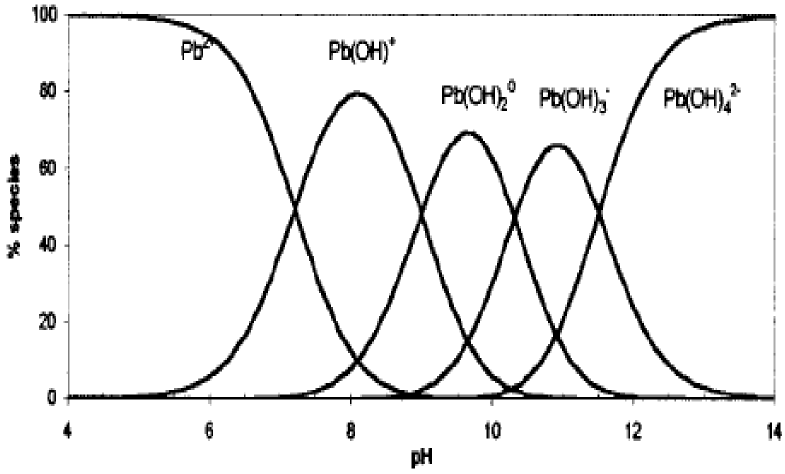


Fig. 2.1 Lead speciation at $[Pb(II)]_t = 10\ \mu M$ [14].

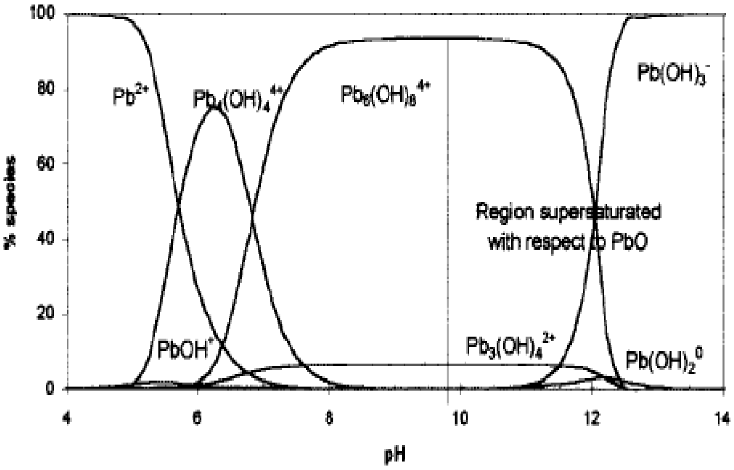


Fig. 2.2 Lead speciation at $[Pb(II)]_t = 0.1$ M [15].

Distribution equations of lead are shown below [16].

$Pb(OH)_2(s) \rightleftharpoons Pb^{2+} + 2OH^-$ $\qquad K_1 = 4.2\times10^{-15}$

$Pb(OH)_2(aq) \rightleftharpoons H + HPbO_2^-$ $\qquad K_2 = 1.2\times10^{-11}$

$Pb(OH)^+ \rightleftharpoons Pb^{2+} + OH^-$ $\qquad K_3 = 1.5\times10^{-8}$

$Pb^{2+} + 2H_2O \rightleftharpoons HPbO_2^- + 3H^+$ $\qquad K_4 = 9.78\times10^{-29}$

$Pb_2(OH)^+ \rightleftharpoons 2Pb^{2+} + OH^-$ $\qquad K_5 = 2.5\times10^{-8}$

$Pb_3(OH)_4^{2+} \rightleftharpoons 3Pb^{2+} + 4OH^-$ $\qquad K_6 = 7.94\times10^{-33}$

$Pb_4(OH)_4^{4+} \rightleftharpoons 4Pb^{2+} + 4OH^-$ $\qquad K_7 = 7.94\times10^{-36}$

$Pb_6(OH)_8^{4+} \rightleftharpoons 6Pb^{2+} + 8OH^-$ $\qquad K_8 = 3.98\times10^{-69}$

From above equations and diagrams, the lead-hydroxide compounds as $Pb(OH)^+$, $Pb_2(OH)^+$, $Pb_3(OH)_4^{2+}$, $Pb_4(OH)_4^{4+}$, $Pb_6(OH)_8^{4+}$, $Pb(OH)_2$ and $HPbO^{2-}$, are observed in the pH range of 4-14.

The structure of hydrated Pb(II) in dilute aqueous solution is investigated. In the hydration shell, the average coordination number is 9 and 24.6 for the first shell and the second shell, respectively. From the result, ligand in the first shell can be exchanged with the second shell and ligand in the second shell can be exchanged with bulk [17].

Pourbaix diagram is a potential pH diagram. In Pourbaix diagram, the pH calculated by equation 2.3 is plotted on the x axis, while the potential *E* calculated by the Nernst equation (equation 2.4) is labeled on y axis.

$$pH = -\log[H^+] \qquad (2.3)$$

$$E = E^0 - \frac{0.0592}{n}\log\frac{[C]^c[D]^d}{[A]^a[B]^b} \qquad (2.4)$$

Fig. 2.3 shows the Pourbaix diagram of lead [18]. This diagram shows the stable form of lead at each point.

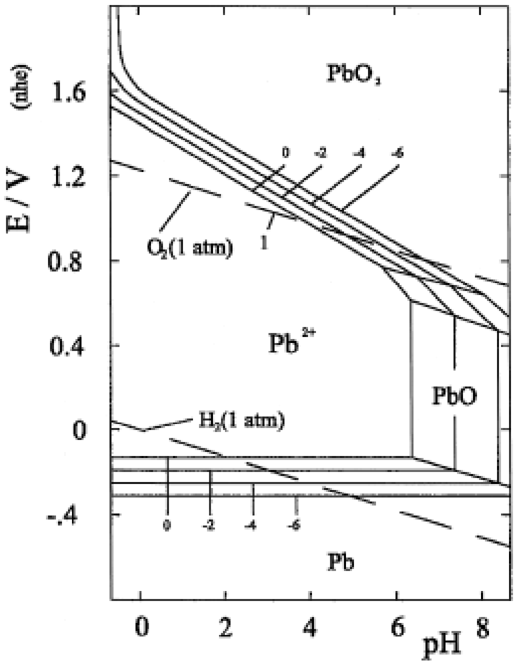


Fig. 2.3 Pourbaix diagram of the lead/water system (0, -2, -4, -6 lines indicate Pb^{2+} concentrations of 1, 10^{-2}, 10^{-4}, 10^{-6} mol/dm^3, respectively).

2.2 Determination of lead

Contamination of lead in water, despite at the low concentration level, remains a major problem to the environment and human health. The Pollution Control Department of Thailand therefore regulates the maximum acceptable concentration (in mg/L) of metals for drinking water [19] and the maximum acceptable concentrations are shown in Table 2.2.

Table 2.2 The maximum acceptable concentration of metals in drinking water

Metals	Maximum acceptable concentration (mg/L)
Arsenic (As)	0.05
Barium (Ba)	1.0
Cadmium (Cd)	0.005
Chromium (Cr)	0.05
Copper (Cu)	1.0
Iron (Fe)	0.3
Lead (Pb)	0.05
Manganese (Mn)	0.05
Mercury (Hg)	0.002
Selenium (Se)	0.01
Silver (Ag)	0.05
Zinc (Zn)	5.0

The determination of Pb(II) concentration in environmental samples, especially in water, is very important. It has been a common interest for researchers and many people. Stripping voltammetry is a direct method for determination of Pb(II) in the water. The potential change will appear when lead analyte forms complex with ligand such as 8-quinolinol [20], 2-acetylpyridine salicyloylhydrazone [21], xylenol orange [22] and S-[*N,N*-bis(carboxymethyl) aminomethyl]-4-methylum belliferone [23]. The advantages of this method are no sample pretreatment process, good sensitivity, portability and low cost.

In the other hand, the spectroscopic techniques such as AAS, ICP-AES or mass spectrometry (MS), have been widely used for determination of metal ions [24-26]. However, the concentration of metal ion is sometime lower than the detection limit of the instruments therefore the preconcentration of sample is required.

Due to the simplicity, convenience and wide scope, the solvent extraction was most studied and widely used in preconcentration step. The difference between the volume of aqueous and organic phases resulted to high-enrichment factor. Dispersive liquid-liquid micro extraction was a method for the preconcentration step [27-28]. The other preconcentration techniques for metal ions such as ion exchange [29], co-precipitation [24], flotation [25] and cloud point extraction [30] were used. Solid phase extraction (SPE) has been widely used for preconcentration of metal ions. SPE has many advantages such as high efficiency, simplicity, rapidity, and less volume of toxic. In order to increase the sensitivity and selectivity for determination of metal ions, the modification of solid phase has widely studied. Table 2.3 shows some of modified solid supports for extraction of Pb(II) and other metals.

Table 2.3 Some modified solid supports for Pb(II) extraction and other metals

Solid support	**Ligand**	**Type of metal extraction**
▶ Sulfur [31]	-	Pb(II), Cd(II)
▶ Ambersorb-572 [26]	EDTA*	Ni(II), Pb(II)
▶ Silica gel [32]	Alizarin violet	Pb(II)
▶ Activated carbons [33]	• DFTD** • DFID*** • MBIP****	Pb(II), Cu(II)
▶ Resin (Pb-Spec®) [34]	Crown ether	Pb(II)
▶ Dowex Optipore [35]	Dibenzyldithio carbamate	Pb(II), Cd(II)

* EDTA = ethylenediaminetetraacedic acid
** DFTD = 5,5-diphenylimidazolidine-2,4-dione (phenytoin)
*** DFID = 5,5-diphenylimidazolidine-2-thione-,4-one (thiophenytoin)
**** MBIP = 2-(4’-methoxy-benzylidenimine)thiophenole

2.3 Adsorption kinetics

The equations of adsorption kinetics are used for explanation of adsorption behavior and adsorption rate of an adsorbent. The pseudo first order equation and the pseudo second order equation are widely used for describe the kinetics of adsorption. A high R^2 value indicates that the model can use for explanation the kinetic adsorption [36].

(1) The pseudo first order kinetic

The equations of the pseudo first order kinetic are followed as:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (2.5)$$

$$\log(q_e - q_t) = \log(q_e) - \frac{kt}{2.303} \qquad (2.6)$$

where:

q_e is the adsorption capacity at equilibrium (mg/g),
q_t is the adsorption capacity at time (mg/g),
k_1 is the rate constant of pseudo first order adsorption (l/min).

The plot of log (q_e-q_t) and t should give a linear relationship which k_1 and q_e can be determined from the slope and the intercept of the plot, respectively.

(2) The pseudo second order kinetic

The equations of the pseudo second order kinetic are followed as:

$$\frac{dq_t}{dt} = k^2 (q_e - q_t)^2 \qquad (2.7)$$

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e} t \qquad (2.8)$$

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + kt \qquad (2.9)$$

$$h = k_2 {q_e}^2 \qquad (2.10)$$

where:

q_e is the adsorption capacity at equilibrium (mg/g),

q_t is the adsorption capacity at time (mg/g),

k_2 is the rate constant of pseudo second order adsorption (g/mg·min),

h is the initial adsorption rate (mg/g min).

The plot of (t/q_t) and t should give a linear relationship which q_e and k_2 can be determined from the slope and the intercept of the plot, respectively.

2.4 Naked-eye detection

The spectrometric methods such as FAAS, ICP-AES and graphite furnace atomic absorption spectroscopy (GFAAS) are widely used for determination of metal ions. These methods provide low detection limit, high sensitivity and selectivity. However these instruments have several limitations for instance high cost operation, time consuming, expensive instrumentation and an expert requirement. Many research groups have developed methods for detection of metal ions without resorting any complicate processes and expensive instrumentation. “Naked-eye detection” is a colorimetric method which appears, decreases color intensities and changes color because of changing absorption wavelength when the anchored ligand molecule interacts with the target analytes. Sometime the ligand used for the naked-eye detection is called sensor molecule. The naked-eye methods using new ligands for metal ion detection were often studied in solution [8, 37-48] while the solid naked-eye method was rarely reported.

From the previous researches, the measured signals for the naked-eye detection were reported in fluorescence intensity and absorbance. Table 2.4 shows some of fluorescence and colorimetric sensors for metal ions naked-eye determination and Table 2.5 shows some of solid sensors for metal ions naked-eye determination.

Table 2.4 Some of fluorescence and colorimetric sensors for metal ions naked-eye determination.

Analyte	**Sensor**	**Matrix**	**Measured signal**		**Interfering ions**
			Fluorescent	**Colorimetric**	
▸ Pb(II) [37]	(2-aminoethyl)bis(2-pyridylmethyl)amine	acetonitrile	✓		Zn(II), Cu(II)
▸ Ca(II), Pb(II) [38]	binaphthyl compounds	methanol	✓		-
▸ Fe(III) [39]	rhodamine B derivertive	ethanol or Tris-HCl aqueous	✓	✓	Cr(III), Fe(III), Cu(II)
▸ Ag(I) [40]	NTTA (FONs)*	aqueous	✓		Hg(I)
▸ Hg(II) [41]	*p*-methoxyphenyl and 1,4-disubstituted 2,3-diaza-1,3-butadienes	acetonitrile/water (7:3) or acetonitrile	✓	✓	-
▸ Hg(II) [42]	DMS1**	THF:water (3:7)	✓	✓	-
▸ Cu(II) [43]	diaminocyclopent-2-enone-based catalytic chemodosimeter	aqueous	✓	✓	-
▸ Hg(II) [44]	8-hydroxyquinoline	dioxane:water (1:3)	✓	✓	Zn(II), Ni(II), Pb(II), Cu(II)
▸ Co(II), Ni(II), Cu(II) [45]	anthracene-9,10-dione based	methanol:water (4:1)		✓	-
▸ Fe(III) [8]	1-(D-glucopyranosyl-2’-deoxy-2’-iminomethyl)-2-hydroxynaphthalene	aqueous		✓	-
▸ Ag(I), Mn(II) [46]	polymeric sensor	THF:water (9:1)	✓(Ag)	✓(Mn)	Co(II), Sr(II)
▸ Pb(II) [47]	diaminoanthraquinone-linked polyazamacro cycles	- MeOH/water (1:1 - DMSO/water (1:1) - aqueous		✓	Cu(II), Cd(II), Al(III)
▸ Pb(II) [48]	G-quadruplex DNAzyme	ABTS*** : H_2O_2		✓	-

* NTTA (FONs) = 5-(3-(2-(naphthalen-3-yloxy)acetyl)thioureido)-1,3,4-thiadiazole-2-carboxylic acid fluorescent organic nanoparticles
**DMS1 = two dithia-dioxa-aza macrocycles on the BODIPY chromophore
***ABTS = 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonicacid)diammoniumsalt

Table 2.5 Some of colorimetric solid sensors for metal ions naked-eye determination.

Metal	Sensor	Detection limit
▸ As(V) [10]	molybdenum-loaded chelating resin having β-hydroxypropyl-di(β-hydroxyethyl)amino moiety	1×10^{-7} M
▸ Hg(II) [49]	silica anchoring porphyrin moiety	1.75×10^{-8} M
▸ Hg(II) [50]	silica nanotube grafted azo-coupled macrocyclic receptor	-
▸ Ag(I), Hg(II), Pb(II) [51]	silica loaded with dithizone and zinc dithizone	-

From the literature reviews, several researches reported the determination of metal ions by the naked-eye detection. The new ligands were synthesized and most of ligands were often studied in solution. The ligands used for Pb(II) naked-eye detection such as (2-aminoethyl) bis(2-pyridylmethyl)amine [37], diaminoanthraquinone-linked polyaza macrocycles [47] and G-quadruplex DNAzyme [48] were reported. But in a practical point of view, the naked-eye detection of metal ions on solid phase was more convenient and simpler method than the liquid systems. The solid naked-eye method was rarely reported, for example molybdenum-loaded chelating resin having β-hydroxy propyl-di(β-hydroxyethyl) amino moiety for As(V) [10], silica anchoring porphyrin moiety [49], silica nanotube grafted azo-coupled macrocyclic receptor for Hg(II) [50] and silica loaded with dithizone and zinc dithizone for Ag(I), Hg(II) and Pb(II) [51].

In this research, a new solid phase used for the naked-eye detection of Pb(II) was prepared. A suitable ligand was selected from dithizone, purpurin, and PAN because these three ligands are complexometric reagents [52], and they were used as a ligand for extraction of Pb(II) and many metal ions [51-58]. Moreover, the modifications of these ligands onto some materials for metal ions extraction and preconcentration were reported. For example, Amberlite XAD-2 functionalized with purpurin exhibited high sorption capacity and high selectivity towards Pb(II) [59]. Amberlite XAD-1180 resin as an adsorbent for Pb-dithizone complex gave high preconcentration factor [60]. Clinoptilolite loaded with PAN was used as an a sorbent for preconcentration of Pb(II), Ni(II), Cd(II) and Cu(II) [52]. PAN was used to apply for several metal ion extraction [53-54]. The colors of PAN complexes with some metal ions in different solvents [54] are shown in Table 2.6.

Table 2.6 Colors of PAN complexes with some metal ions in water, amyl alcohol and CCl_4

Ions	**Color in water**	**Color in amyl alcohol**	**Color in CCl_4**
H_2O	yellow	yellow	yellow
Bi(III)	pink	yellow	pink
Cd(II)	red	red	red
Cu(II)	deep red	red	yellow
Pd	green	green	green
Pt	red	red	-
Sn(II)	pink	yellow	yellow
Hg(II)	red	yellow	yellow
Co(II)	brownish red	green	green
Pb(II)	red	red	yellow
Fe(II)	red	-	-
Fe(III)	dark red	red	yellow
Ni(II)	red	red	red
Zn(II)	bright pink	red	red

PAN was used as a ligand for modification on several materials for various metal ions. The optimum pH of solution depended on type of metal ions. Some modifications of PAN onto various materials for determination of various metal ions are listed in Table 2.7.

Table 2.7 Modifications of PAN onto various materials and their applications

Materials	**Metal**	**pH**
Loaded on clinoptilolite [52]	Pb, Ni, Cd and Cu	8.5
Modified on polymeric membranes [53]	Zn	2-8
Modified on C18-cartridge [54]	Ce, Dy, La, Sm, and Y	8
Anchored to silica nanoparticle [61]	Cd	9.2-10
Immobilized on surfactant-coated alumina [62]	Co	4.5
Modified on naphthalene [63]	Mn	8.8–10.8
Impregnated on ambersorb 563 resin [64]	Cu, Ni, Cd, Pb, Cr and Co	9

Therefore, this work focused on the preparation of silica gel coated with a suitable ligand and on the determination of Pb(II) in aqueous solution by the naked-eye method after batch extraction.

CHAPTER III

EXPERIMENTAL SECTION

3.1 Chemicals

All used chemicals and reagents were of analytical grade and are listed in Table 3.1.

Table 3.1 Chemicals and reagent list

Chemicals	Supplier
Calcium nitrate tetrahydrate	Riedel-de Haen
Dichloromethane	Carlo Erba
Dithizone	May&Baker Ltd
Ethanol	Merck
Magnesium nitrate	Fluka
Nitric acid 65%	Merck
Potassium nitrate	BDH
1,2-(Pyridylazo)-2-naphthol (PAN)	Fluka
Silica gel (0.063-0.200 mm)	Merck
Sodium hydroxide	Carlo Erba
Sodium nitrate	Carlo Erba
Cadmium standard solution (1,000 mg/L)	Merck
Cobalt standard solution (1,000 mg/L)	Fisher Scientific
Copper standard solution (1,000 mg/L)	Merck
Gold standard solution (1,000 mg/L)	Merck
Iron standard solution (1,000 mg/L)	Fisher Scientific
Lead standard solution (1,000 mg/L)	Merck
Manganese standard solution (1,000 mg/L)	Fisher Scientific
Silver standard solution (1,000 mg/L)	Merck
Zinc standard solution (1,000 mg/L)	BDH

3.2 Apparatus

- **Inductively-coupled plasma atomic emission spectrometer (ICP-AES)**

The concentration of lead in an aqueous solution was determined by an inductively-coupled plasma atomic emission spectrometer (ICP-AES) model iCAP 6000 series (Thermo scientific). The operating conditions are listed in Table 3.2.

Table 3.2 ICP-AES operating conditions for determination of lead in a solution

Operating conditions	
Wavelength (nm)	220.3
Flush pump rate (rpm)	50
Analysis pump rate (rpm)	50
RF power (W)	1150
Auxiliary gas flow (L/min)	0.5
Nebulizer gas flow (L/min)	0.5
Coolant gas flow (L/min)	12

- **Flame atomic absorption spectrometer (FAAS)**

The concentration of lead in an aqueous solution was determined by a flame atomic absorption spectrometer (FAAS) model AAnalyst 100 (Perkin Elmer). The operating conditions are listed in Table 3.3.

Table 3.3 FAAS operating conditions for determination of lead in a solution

Operating conditions	
Wavelength (nm)	283.3
Slit width (nm)	0.70
Lamp type	Hollow Cathode Lamp
Lamp current (mA)	10
C_2H_2 flow rate (mL/min)	2
Air flow rate (mL/min)	4

- **Diffuse reflectance ultraviolet visible spectrophotometer (DR-UV-vis)**

A diffuse reflectance ultraviolet visible spectrophotometer (DR-UV-vis) supported by UV-2500PC (Shimadzu) was used for characterization of silica gel after coating with PAN or Si-PAN.

- **pH meter**

The pH values of solution were measured by a Metrohm pH meter model 744.

- **Centrifuge**

The centrifuge Centaur2 (Sanyo®) was used for separation the solid phase from the solution in batch experiment.

3.3 Preparation of solid phase

3.3.1 Coating of ligand onto silica gel

Ligands used in this research included dithizone, purpurin and PAN. In a 100 mL round-bottomed flask, 2 g of silica gel and 20 mL of dithizone solution (5 mM in dichloromethane) were magnetically stirred for 5 hr at room temperature. Then the suspension was filtered and dried at room temperature until dryness. The Si-dithizone product was kept in a desiccator before use. Si-purpurin and Si-PAN were also prepared in the same manner described above. Purpurin and PAN were dissolved in ethanol.

3.3.2 Stirring time

In a 100 mL round-bottomed flask, 2 g of silica gel was magnetically stirred with 20 mL of 5 mM PAN in ethanol at room temperature. The stirring time was varied from 0.5 to 5.0 hr. Then the suspension was filtered and dried at room temperature until dryness. The PAN coating efficiency onto silica gel was investigated by DR-UV-vis spectrophotometer at 468 nm.

3.3.3 Amount of silica gel

In a 100 mL round-bottomed flask, an amount of silica gel was magnetically stirred with 20 mL of 5 mM PAN in ethanol at room temperature. The amount of silica gel studied was varied from 1 to 4 g. Then the suspension was filtered and dried at room temperature until dryness. The PAN coating efficiency onto silica gel was investigated by DR-UV-vis spectrophotometer at 468 nm.

3.3.4 Concentration of PAN

PAN solution was prepared by dissolving an appropriate amount of PAN in ethanol to obtain 1-10 mM. 2 g of silica gel and 20 mL of PAN solution of known concentration were magnetically stirred in a round-bottomed flask at room temperature for 1 hr. Then the suspension was filtered and dried at room temperature until dryness. The products Si-PAN (1 mM), Si-PAN (3 mM), Si-PAN (5 mM), Si-PAN (8 mM) and Si-PAN (10 mM) were kept in a desiccator before use. The PAN coating efficiency onto silica gel (Si-PAN) was investigated by DR-UV-vis spectrophotometer at 468 nm.

3.4 Preliminary test for naked-eye detection of metal ions

The naked-eye detection of metal ions e.g. Zn(II), Cu(II), Au(II), Mn(II), Cd(II), Co(II), Ag(I), Fe(III) and Pb(II) after batch extraction with Si-PAN was studied. The pH of solution containing 5 mg/L metal ion was adjusted with 1% HNO_3 and 1% NaOH to pH 3, 6, and 9. 20 mg of Si-PAN was mixed with 5.0 mL of metal ion solution in a test tube. The mixture was magnetically stirred at room temperature for 30 min. The solid phase was separated from the solution by centrifugation at 2,000-2,500 rpm for 5 min. The residue metal concentration was determined by FAAS. The color of Si-PAN after extraction was considered by naked-eye assay.

3.5 Extraction of Pb(II)

The working solution of Pb(II) was diluted from a stock solution of 1,000 mg/L to the required concentration. All working solutions were freshly prepared with deionized water (DI) or Milli-Q water. The extraction study was investigated on batch system and all experiments were carried out for triplicates.

3.5.1 Effect of pH

The pH of Pb(II) solution (5 mg/L) was adjusted to pH values ranging from 2.5 to 5.5 with various concentrations of HNO_3 and NaOH solutions. Si-PAN (20 mg) was magnetically stirred with 5.0 mL of Pb(II) solution in a test tube for 30 min at room temperature. Then the mixture was separated by centrifugation at 2,000-2,500 rpm for 5 min. The residue concentration of Pb(II) in the solution was determined by FAAS.

3.5.2 Effect of contact time

The contact time between Si-PAN and Pb(II) solution of known concentration was studied in a range of 1 to 60 min. 20 mg of Si-PAN and 5.0 mL of Pb(II) solution (5 mg/L) at the optimum pH were mixed in a test tube and were magnetically stirred at room temperature. Then the mixture was separated by centrifugation at 2,000-2,500 rpm for 5 min. The residue concentration of Pb(II) in the solution was determined by FAAS.

3.6 Naked-eye detection of Pb(II)

3.6.1 Concentration of Pb(II)

The limit of the naked-eye detection of Pb(II) was investigated by varying the concentrations of Pb(II) from 10 mg/L to the lowest concentration. 5.0 mL of Pb(II) solution of known concentration at the optimum pH and 20 mg of Si-PAN coating with 5 mM of PAN (or Si-PAN (5 mM)) were magnetically stirred in a test tube for

10 min at room temperature. Then the suspension was separated by centrifugation at 2,000-2,500 rpm for 5 min. The Si-PAN was dried until dryness. Then the change in the color of Si-PAN (5 mM) was observed by naked-eye assay.

3.6.2 Interfering ions

The solution containing the interfering ions such as Na^+, K^+, Mg^{2+}, and Ca^{2+} (1,000 mg/L) was prepared by dissolving the solid of $NaNO_3$, KNO_3, $Mg(NO_3)_2{\cdot}6H_2O$ and $Ca(NO_3)_2$ in Milli-Q water. The working solution of Pb(II) was diluted from the stock solution of Pb(II) (1,000 mg/L) with Milli-Q water to the required concentration. In part of Ni(II), Zn(II), Cu(II), Fe(III), Mn(II), Cd(II), Co(II), Ag(I) and Pb(II) solutions, the working solution was diluted from stock solution (1,000 mg/L) to the required concentration with Milli-Q water.

The solution of interfering ion (25.0 mL) spiked with 200.0 µL of 100 mg/L Pb(II) solution were adjusted to the optimum pH with 1% HNO_3 and 1% NaOH. 5.0 mL of these solutions were added to a test tube containing 20 mg of Si-PAN (0.5 mM). The suspension was magnetically stirred at room temperature for 10 min and then separated by centrifugation at 2,000-2,500 rpm for 5 min. The concentration of Pb(II) before and after extraction were determined by ICP-AES. Si-PAN was dried until dryness and its color change was detected by naked-eye assay.

3.7 Shelf life of Si-PAN

Si-PAN was kept in an amber bottle under room temperature in a dessicator. The shelf life of Si-PAN was studied for 12 weeks. Its extraction efficiency was examined once a week for 12 weeks. 20 mg of Si-PAN and 5.0 mL of Pb(II) solution (0.8 mg/L) at the optimum conditions were mixed in a test tube and magnetically stirred at room temperature. Then the mixture was separated by centrifugation at 2,000-2,500 rpm for 5 min. The residue concentration of Pb(II) in the solutions was determined by ICP-AES and the change in color of Si-PAN was also detected by naked-eye assay.

3.8 Determination of lead in real sample

The extraction efficiency of Pb(II) in spiked solution and unspiked solution were compared. In this work, 4 brands of drinking water were studied as real samples. 25.0 mL of real sample spiked with 200.0 μL of 100 mg/L Pb(II) was adjusted the pH to 5 with 1% HNO_3 and 1% NaOH. 5.0 mL of these solutions were added into a test tube containing 20 mg of Si-PAN (0.5 mM). The suspension was magnetically stirred at room temperature for 10 min and then separated by centrifugation at 2,000-2,500 rpm for 5 min. The residue concentration of Pb(II) in the solutions before and after extraction was determined by ICP-AES and the change in color of Si-PAN was detected by naked-eye assay.

CHAPTER IV

RESULTS AND DISCUSSION

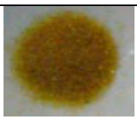
This chapter presents the optimum conditions for preparation of Si-ligand. The parameters affected to Pb(II) extraction such as pH of solution and the contact time between the solution and Si-ligand were presented. The influence of the concentration of ligand and the concentration of Pb(II) to lead naked-eye detection were discussed. The effect of the interfering ions and the shelf life were also studied. Finally, the determination of Pb(II) by naked-eye detection in real sample was presented.

4.1 Preparation of Si-ligand

Silica gel was chosen as a solid support for this work because silica gel is white material and the modification onto the surface of silica gel is a widely used technique. For the naked-eye detection, the color of complex should be visible and should differ from the color of ligand. Dithizone, purpurin and PAN are complexometric reagents and they were used as ligand for extraction of Pb(II) and many metal ions. Therefore, the ligands used for coating to silica gel in this work as dithizone, purpurin and PAN were chosen for coating onto silica gel.

Silica gel coated with dithizone, purpurin and PAN were called Si-dithizone, Si-purpurin and Si-PAN, respectively. The color of silica gel after coating with ligands was changed to different colors. The color of Si-dithizone, Si-purpurin and Si-PAN are shown in Table 4.1.

Table 4.1 Colors of Si-dithizone, Si-purpurin and Si-PAN

Solid phase	**Color**	
Si-dithizone		dark brown
Si-purpurin		light brown
Si-PAN		orange

The colors of Si-dithizone, Si-purpurin and Si-PAN were dark brown, light brown and orange, respectively. The suitable ligand for Pb(II) naked-eye detection was preliminarily considered from its extraction efficiency. The Pb(II) extraction efficiency from an aqueous solution was reported in term of percent extraction (%E) according to equation 4.1 as follows:

$$\%\ \text{Extraction} \quad = \quad \frac{C_i - C_f}{C_i} \times 100 \qquad (4.1.)$$

where:

C_i is the initial concentration of Pb(II) (mg/L)

C_f is the residual concentration of Pb(II) after extraction (mg/L).

The Si-ligand (Si-dithizone, Si-purpurin and Si-PAN) were used as an adsorbent for extraction of 5 mg/L of Pb(II) solution. The Pb(II) extraction with Si-ligand was compared with Pb(II) extraction with silica gel without ligand and the color of Si-ligand after extraction (called Si-ligand-Pb) was also considered by naked-eye detection.

The percentages of Pb(II) extraction using Si-dithizone, Si-purpurin, Si-PAN in comparison with silica gel are illustrated in Fig. 4.1.

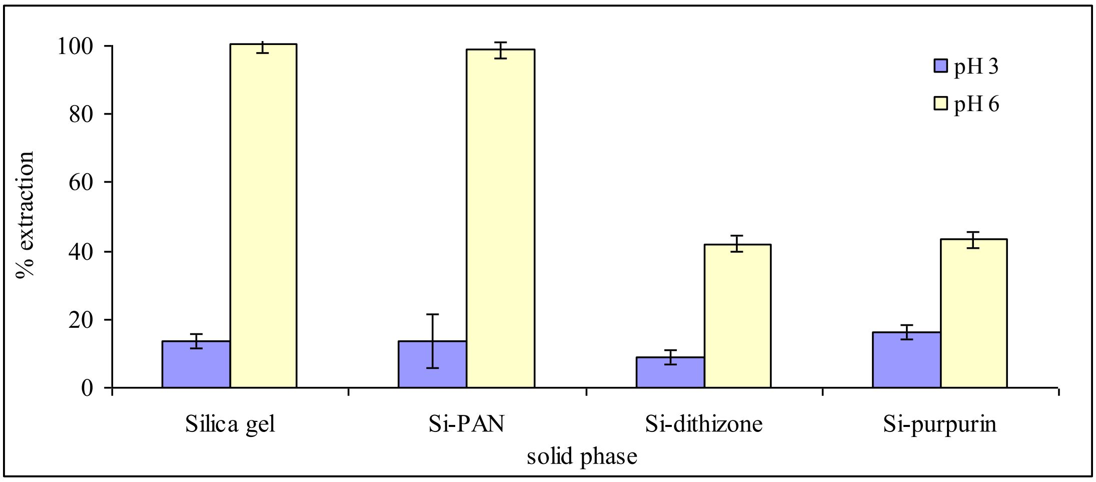
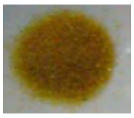
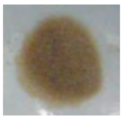
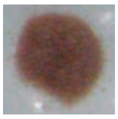


Fig.4.1 Percent extraction of Pb(II) with silica gel, Si-PAN, Si-dithizone and Si-purpurin at pH 3 and pH 6 (n=3).

It was found that all solid phases were able to extract Pb(II) from aqueous solutions. The Pb(II) extraction efficiency for all solid phases at pH 6 was higher than at pH 3 because the binding sites of ligands were protonated at pH 3 due to their pKa values (pKa of PAN = 2.91, pK_a of dithizone = 5.31 [65] and pK_a of purpurin = 7.05 [65]). At pH 6, the quantitative extraction of Pb(II) with Si-PAN (≥95%) was obtained while the percentage of the extraction of 50 was obtained for Si-dithizone and Si-purpurin. It was probably due to the difference of the percent loading of each ligand onto silica gel.

Table 4.2 shows the colors of Si-ligand and Si-ligand after extraction of Pb(II) (Si-ligand-Pb) at pH 3 and pH 6.

Table 4.2 Colors of Si-ligand and Si-ligand-Pb at pH 3 and pH 6

Si-ligand	**Color**		
	Si-ligand	**Si-ligand-Pb at pH3**	**Si-ligand-Pb at pH6**
Si-dithizone	 dark brown	 light yellow	 brown
Si-purpurin	 light brown	 light pink	 light pink
Si-PAN	 orange	 yellow	 dark pink

From the naked-eye investigation, it was found that the intensity of the color depended on the percent extraction. The intensity of color increased with the increase of percent extraction. The color of Si-dithizone-Pb at pH 3 was light yellow and at pH 6 the color of Si-dithizone-Pb was brown. The color of Si-purpurin-Pb was light pink at pH 3 and pH 6. The colors of Si-dithizone-Pb and Si-purpurin-Pb changed in the same shade of color but the color of Si-PAN-Pb changed to the different tone. The colors of Si-PAN-Pb changed from orange to yellow and dark pink at pH 3 and pH 6, respectively. Because of a high percentage of Pb(II) extraction and a color change of Si-ligand after extraction, Si-PAN was chosen as a solid phase for extraction of Pb(II) in aqueous solution for the further experiments.

- Characterization of Si-PAN

For non-transparent material, it needs to analyze by scattering or reflection of light. The Kubelka-Munk equation is an equation that explains the reflection and diffusion of solid. The Kubelka-Munk equations show linear relationship for spectral intensity relative to sample concentration [66]. The Kubelka-Munk equations are shown in equation 4.2-4.4 as follows.

$$A = -\log R \qquad (4.2)$$

$$f(R) = \frac{(1-R)^2}{2R} = \frac{\varepsilon}{S} \qquad (4.3)$$

$$C = -\frac{S}{\varepsilon} + \frac{S}{2\varepsilon}R + \frac{S}{2\varepsilon}R^{-1} \qquad (4.4)$$

where:

A is the absorbance,
C is the concentration,
R is the absolute reflectance of the sample,
ε is the molar absorption coefficient,
S is the scattering coefficient.

The coating of PAN onto silica gel was investigated from the DR UV-vis spectrophotometer in the range of wavelength of 200-800 nm. The maximum absolute reflectance of Si-PAN was observed at around 468 nm corresponding to azo group while the reflectance of silica gel was not found at the same wavelength. Therefore, the DR UV-vis absorption was measured at 468 nm to investigate the coating efficiency of Si-PAN.

4.1.1 Stirring time

The optimum stirring time for coating PAN onto silica gel was studied in the range of 0.5-5 hr. The coating efficiency was investigated from the DR UV-vis absorption of Si-PAN at 468 nm. The f(R) of Si-PAN at different stirring times is shown in Fig. 4.2.

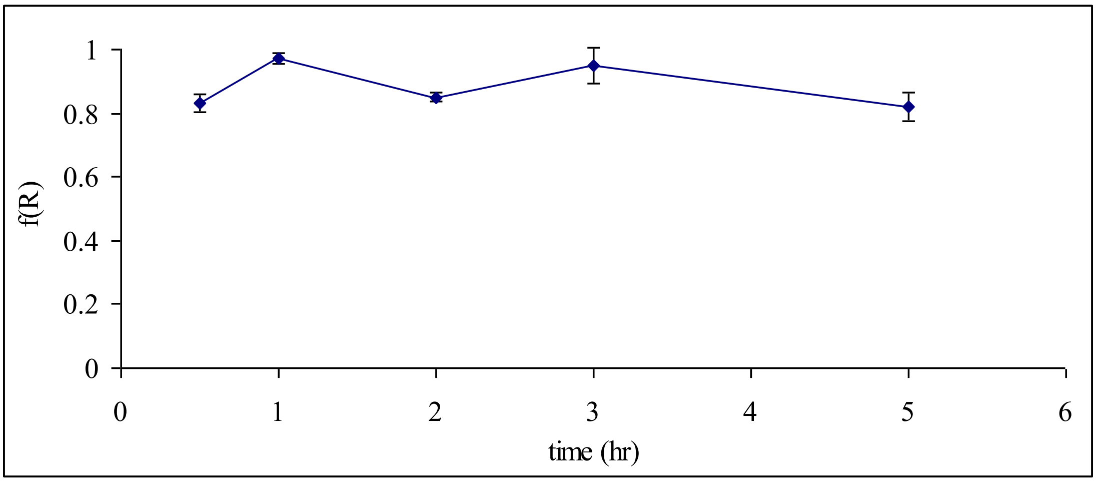


Fig. 4.2 The f(R) of Si-PAN at 468 nm in a function of the stirring time between silica gel and PAN solution.

From the results, the insignificant difference of the signal for the stirring time between 0.5-5 hr was obtained (calculated by student's pair t-test). The increase of stirring time increased insignificant reflectance. For the further studies, the stirring time of silica gel and PAN solution to obtain the maximum loading (under these conditions: 2 g of silica gel and 20 mL of 5 mM PAN solution) was 1 hr.

4.1.2 Amount of silica gel

The amount of silica gel coated with PAN was studied in the range of 1- 4 g to determine the maximum amount of silica gel coated with 20 mL of 5 mM PAN solution. The DR-UV-vis absorption of Si-PAN was investigated to indicate the coating efficiency. The results are shown in Fig. 4.3.

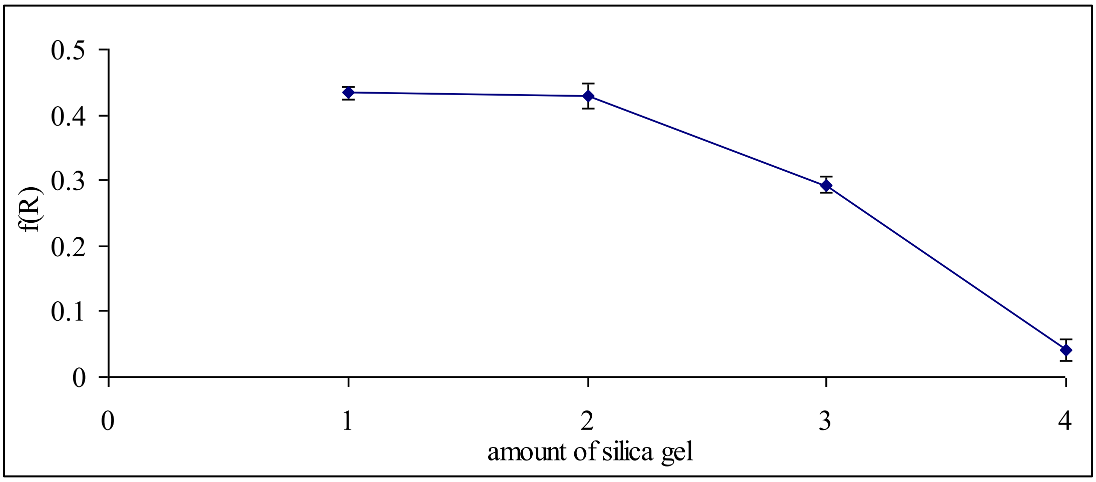


Fig.4.3 The f(R) of Si-PAN at 468 nm in a function of the amount of silica gel.

The signal of Si-PAN decreased with increase of the amount of silica gel. The insignificant difference (calculated by pair student's t-test: t_{cal} = 0.0157 and $t_{critical}$ = 0.4518) of the signal for 1-2 g of silica gel was obtained. But the significant difference of the signal between 2-3 g of silica gel was observed (calculated by pair student's t-test: t_{cal} = 0.9811 and $t_{critical}$ = 0.3228). For further coating PAN onto silica gel, 2 g of silica gel was used to obtain the maximum loading with 20 mL of 5 mM PAN solution.

4.1.3 Concentration of PAN

In order to study the color change of Si-PAN after the extraction of Pb(II) from aqueous solution, the maximum amount of PAN for coating onto silica gel was studied. The percent extraction of Pb(II) depended on the amount of PAN on silica gel. The increase of PAN on silica gel should increase percent extraction of Pb(II). Therefore, the concentration of PAN was studied in the range of 1-10 mM. The PAN coating efficiency onto silica gel was investigated by the DR-UV-vis spectrophotometer at 468 nm.

The absolute reflectance spectra of Si-PAN at different concentrations of PAN are shown in Fig. 4.4 and the signal at 468 nm of Si-PAN at different concentrations of PAN is shown in Fig. 4.5.

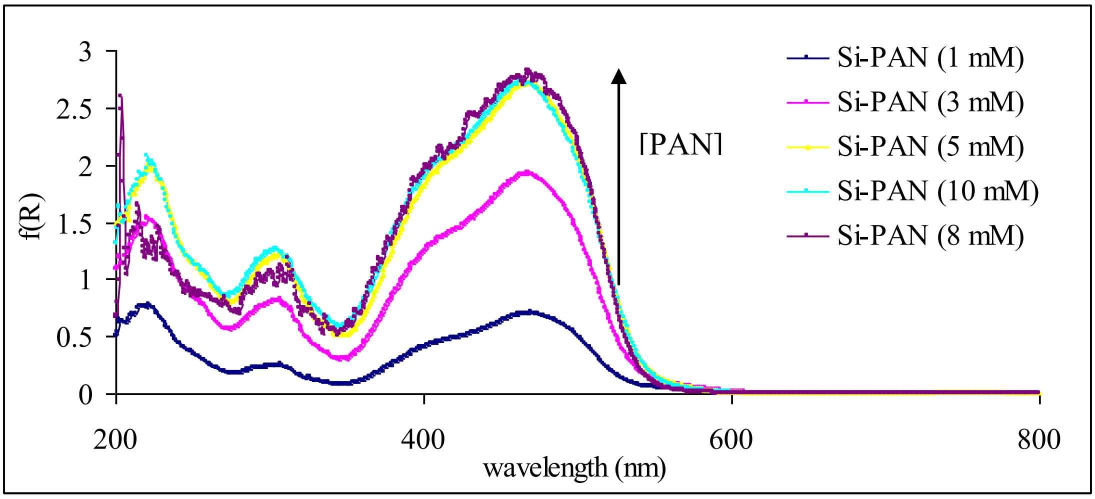


Fig.4.4 The f(R) spectra of Si-PAN at 1-10 mM of PAN.

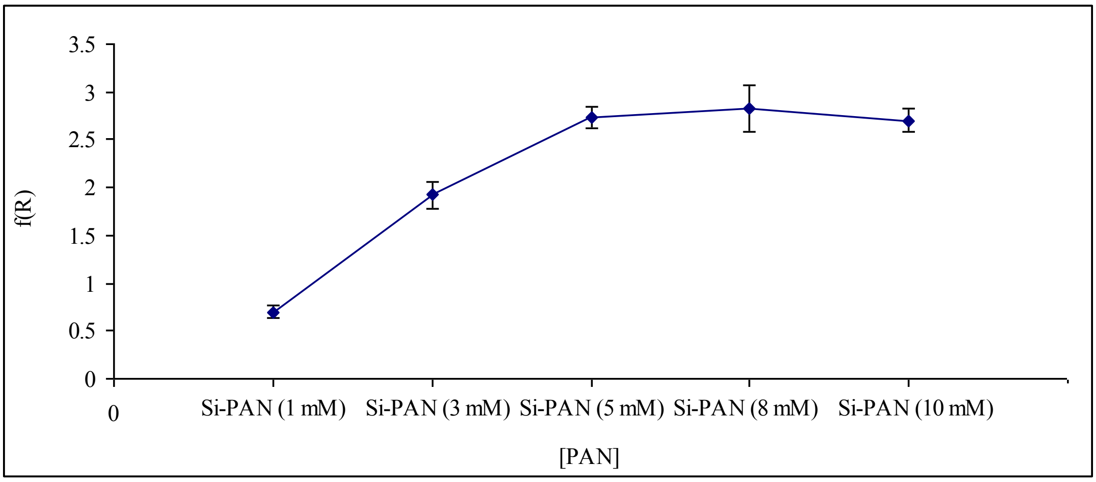


Fig.4.5 The f(R) of Si-PAN of 1-10 mM PAN at 468 nm.

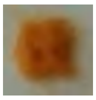
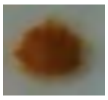
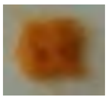
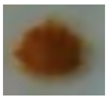
The f(R) of Si-PAN at 468 nm increased with increase of the concentration of PAN. The maximum f(R) was found to reach equilibrium when the concentration of PAN was 5 mM. This indicated that PAN was coated onto silica gel in monolayer type. The interaction between silica gel and PAN was probably both hydrogen bonding and physisorption. Therefore, the optimum concentration of PAN for coating onto 2 g of silica gel was 5 mM and this condition was used in the further studies.

4.2 Preliminary test for naked-eye detection

PAN may be used as an indicator for metal ions such as zinc, copper, cadmium, etc. Most complexes formed reddish colored chelates, but cobalt and palladium formed greenish colored chelates [54].

In order to test the colorimetric property of Si-PAN, the preliminary test for metal ions naked-eye detection as Zn(II), Cu(II), Au(III), Mn(II), Cd(II), Co(II), Ag(I), Fe(III) and Pb(II) was studied. The concentration of metal ions was fixed and the pH of solution was adjusted to acidic solution (pH about 3), neutral solution (pH about 6) and basic solution (pH about 9). The color of Si-PAN after batch extraction of various metal ions from aqueous solution and the percentage of metal extractions are shown in Table 4.3.

Table 4.3 Percent extractions and colors of Si-PAN after batch extraction of various metal ions (the color of Si-PAN-Metal obtained from the highest extraction)

Metal ions	pH	% extraction	Si-PAN	Si-PAN-Metal*
Zn(II)	2.9	30		
	6.1	76		
	9.2	93	orange	reddish pink
Cu(II)	3.0	1		
	6.0	13		
	9.1	97	orange	reddish purple
Au(III)	3.1	36		
	6.1	21		
	9.1	21	orange	brown
Mn(II)	3.0	3		
	6.2	15		dark brown
	8.7	40	orange	
Cd(II)	3.0	0		
	6.1	30		
	9.1	38	orange	light purple
Co(II)	3.1	13		
	6.0	16		
	9.0	26	orange	dark green
Ag(I)	3.0	46		
	6.0	30		
	9.0	0	orange	brown
Fe(III)	3.0	41		
	6.0	95		
	9.0	precipitate	orange	light pink
Pb(II)	3.0	0		
	6.9	93		
	9.0	precipitate	orange	pink

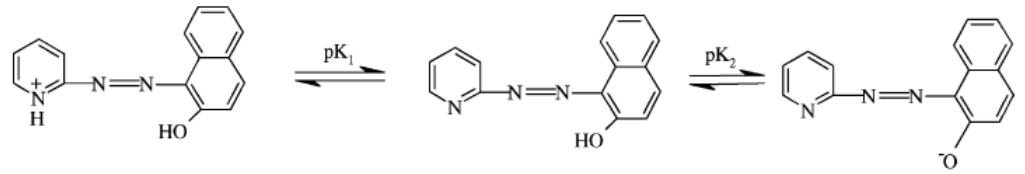
Various metal ions were extracted from aqueous solutions by Si-PAN at pH 3 to 9 and various colors of complex form were observed by naked-eye assay. The high percent extractions of several metal ions e.g. Zn(II), Cu(II), Mn(III), Cd(II) and Co(II) with Si-PAN were observed at basic solution because in the basic solution PAN existed in fully deprotonated form. Ag(I) and Au(III) was extracted at acid solution higher than basic solution probably due to the anionic formation of Ag(I) and Au(III). The colors of Si-PAN after extraction of metal ions were categorized to 3 groups: red, brown and green. The color of Si-PAN after Zn(II), Cu(II), Fe(III), Cd(II) and Pb(II) extraction was red. The complexes of Si-PAN and Au(III), Mn(II), and Ag(I) were brown and Si-PAN-Co was green. These indicated that PAN can be used as a solid sensor for several metal ions and gave the various color of complex. Although the colors of Si-PAN-Zn and Si-PAN-Cu were attracted because of high percent extraction and high intensity of color changed. But the high percent extraction was observed at basic solution in which SiO_2 can be dissolved. The interesting points were high percent extraction of Pb(II) at pH 6 and the color change of Si-PAN-Pb observed with naked-eye assay. Therefore, Si-PAN was chosen to study as a solid sensor for Pb(II) naked-eye detection to improve a simple method for detection of Pb(II) in the drinking water. The conditions for extraction of Pb(II) were optimized in the next experiment.

4.3 Extraction of Pb(II)

Si-PAN was used for extraction of Pb(II) in aqueous solution. The color intensity of Si-PAN-Pb depended on percent extraction of Pb therefore the efficiency of Pb(II) extraction was important. The efficiency of extraction was reported in term of percent extraction according to the equation 4.1. The parameters affected to the extraction efficiency including pH of Pb(II) solution and contact time between the solution and the Si-PAN were studied.

4.3.1 Effect of pH

The pH of solution was the first parameter in the extraction study. The extraction efficiency of Pb(II) onto Si-PAN as a function of pH was studied in batch method. The pH of solution can affect to the surface charge of Si-PAN because PAN exists in different forms at different pH of solution. In acidic solution (pH ≤ 2), PAN exists in the water-soluble yellow-green protonated LH_2^+ ions. Between pH 3-11, PAN exists as the neutral LH molecule, soluble in organic solvents to give a yellow color. In alkaline solutions (pH ≥ 11), PAN exists as the water-soluble red L^- anions [67-68]. The structures of PAN molecule in different form are shown below.



LH_2^+(yellow-green) LH (yellow) L^- (red)

Moreover, at different pH of solution, lead exists in different forms. In acidic solution lead exists in Pb^{2+}. In solutions pH more than 6.5, the precipitation of the hydroxyl compound of Pb(II) occurs [16-17]. In addition, silica gel can dissolve in the basic solution. From these reasons, the extraction of Pb(II) in aqueous solution with Si-PAN was studied in the pH range of 2.5-5.5 and the results are illustrated in Fig. 4.6.

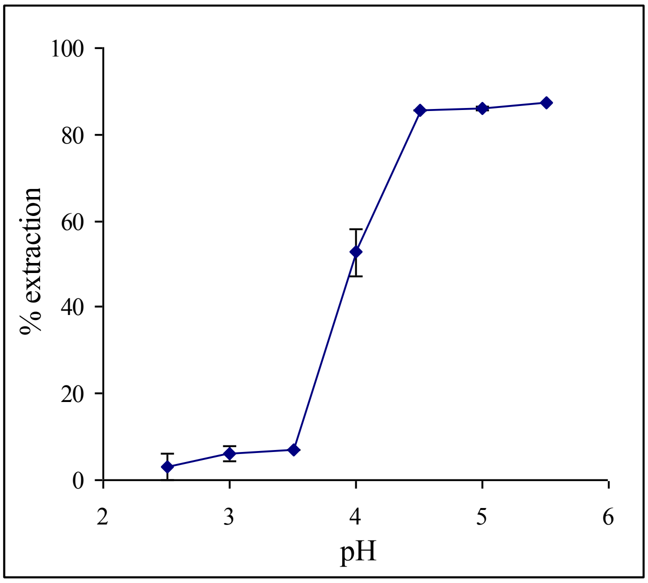


Fig. 4.6 Effect of pH to percent extraction of Pb(II).

The percent extraction of Pb(II) was less than 5% at the pH range of 2.5-3.5 because the binding sites of PAN were protonated. When the pH increased, the protonation of PAN molecules decreased whereas the Pb(II) extraction increased from 5% to more than 80% with increasing the solution pH from 3.5 to 4.5. Moreover, the color of sorbent (Si-PAN) changed from orange to light pink (Si-PAN-Pb), but the color change of Si-PAN was not observed under pH 2.5-5.5. The maximum percentage of Pb(II) extraction was found at the pH range of 4.5-5.5. Therefore, the solution pH of 5 was chosen as the optimum pH to extract Pb(II).

As PAN is a tridentate ligand complexing with metal ions through the hydroxyl oxygen atom, pyridine nitrogen atom, and one of the azo group nitrogen atoms [67], the complex formation between Pb(II) and PAN was proposed as shown in Fig. 4.7.

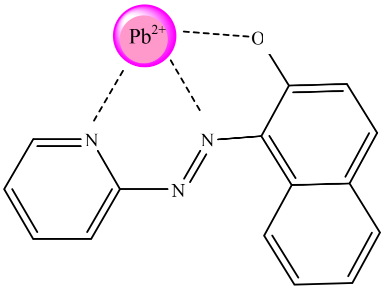


Fig. 4.7 Proposed complex formation between Pb(II) and PAN.

The f(R) spectra of Si-PAN and Si-PAN-Pb were investigated and illustrated in Fig. 4.8. It was found that f(R) of Si-PAN-Pb was differed with f(R) of Si-PAN. The signal at 468 nm decreased with increase of the signal at 580 nm. It was indicated that the electrons shift to red shift were performed from the complexation between Si-PAN and Pb(II). Therefore, the signal of Si-PAN-Pb at 580 nm was the characteristic wavelength of the complex between PAN and Pb(II).

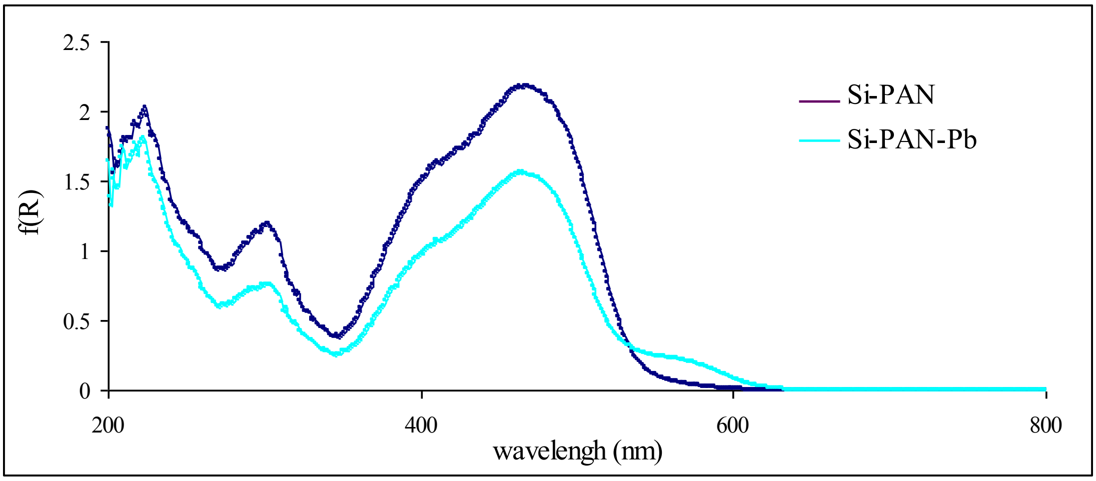


Fig. 4.8 The f(R) spectra of Si-PAN and Si-PAN-Pb at pH 5.

4.3.2 Effect of contact time

The Pb(II) extraction equilibrium was studied and reported in term of percent extraction with different contact times between Si-PAN and a Pb(II) solution. The study of the optimum contact time was carried out in the range of 1-60 min under the optimum pH of 5 with batch experiments. The initial concentration of Pb(II) in aqueous solution was fixed at 5 mg/L. The results are illustrated in Fig. 4.9.

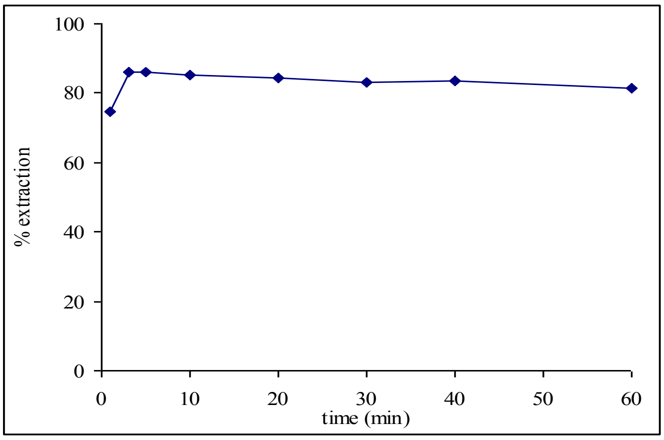


Fig. 4.9 Effect of contact time to percent extraction of Pb(II)**.**

Si-PAN showed the fast kinetics due to it required only 5 min to reach equilibrium. The contact time of 10 min was used for the further studies. To explain the kinetic of adsorption, the pseudo first order model and pseudo second order model were studied. Fig. 4.10 and 4.11 show the pseudo first order model and the pseudo second order model of Pb(II) adsorption, respectively.

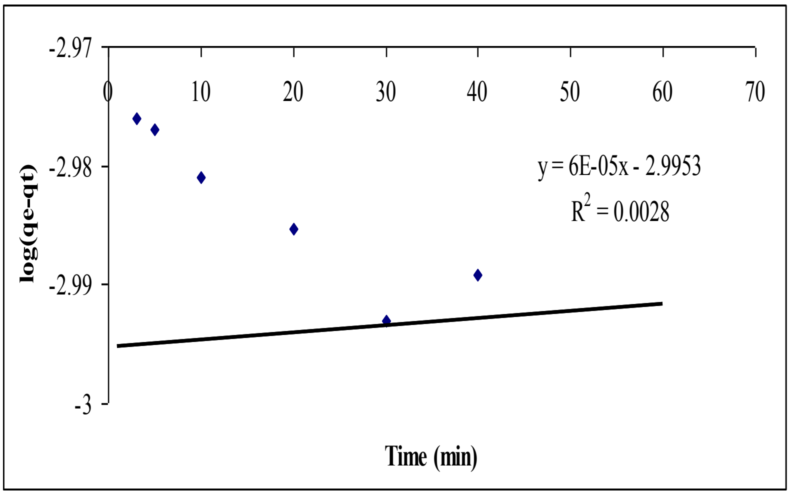


Fig. 4.10 The pseudo first order plot of adsorption of Pb(II).

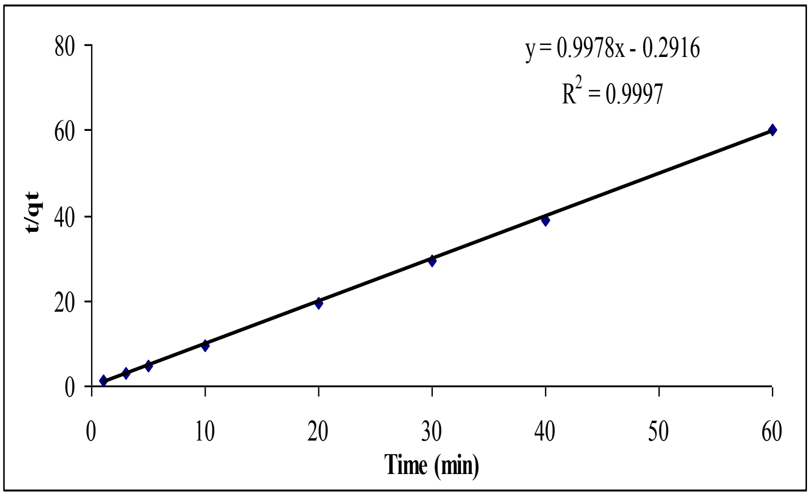


Fig. 4.11 The pseudo second order plot of adsorption of Pb(II).

The R^2 values (correlation coefficient) of the pseudo first order model and the pseudo second order model were compared. The plot showed that R^2 of the pseudo first order model was 0.0028 while R^2 of the pseudo second order model was 0.9997. The correlation coefficient of the pseudo second order model was close to 1 indicating that the adsorption of Pb(II) fit with the pseudo second order model. Moreover, the other kinetic constants were calculated from the plot. From the pseudo second order model, the initial adsorption rate h was 1.0022 (mg/g min) and the rate constant k_2 was 11.78 (g/mg·min).

4.4 Naked-eye detection of Pb(II)

In this work, the parameters affected to the color change of Si-PAN after the extraction were studied such as concentration of Pb(II) and interfering ions.

4.4.1 Concentration of Pb(II)

The lowest concentration of Pb(II) detectable with the Si-PAN (5 mM) by naked-eye detection was studied under the optimum conditions as follows: pH of solution = 5 and contact time = 10 min. The concentration of Pb(II) was varied in a range of 0-10 mg/L. After batch extraction, the color change of Si-PAN was investigated and the results are shown in Table 4.4.

Table 4.4 Colors of Si-PAN-Pb after extraction at different concentrations of Pb(II)

Concentration of Pb(II) (mg/L)	**Color of Si-PAN-Pb**	
0		**orange**
0.01		**orange**
0.05		**orange**
1		**orange**
5		**light pink**
10		**light pink**

The colors of Si-PAN-Pb in function of Pb(II) concentration were compared with the color of Si-PAN (5 mM). It was found that the color of Si-PAN (5 mM) was visibly changed when the concentrations of Pb(II) were 5 and 10 mg/L. At the concentration of Pb(II) lower than 5 mg/L, the color change was not detected by naked-eye. Moreover, DR UV-vis absorption of Si-PAN-Pb at different concentrations of Pb(II) was measured by DR-UV-vis spectrophotometer. The f(R) of Si-PAN-Pb spectra at different concentrations of Pb(II) are shown in Fig. 4.12 and the f(R) values at 468 nm and 580 nm are shown in Fig 4.13.

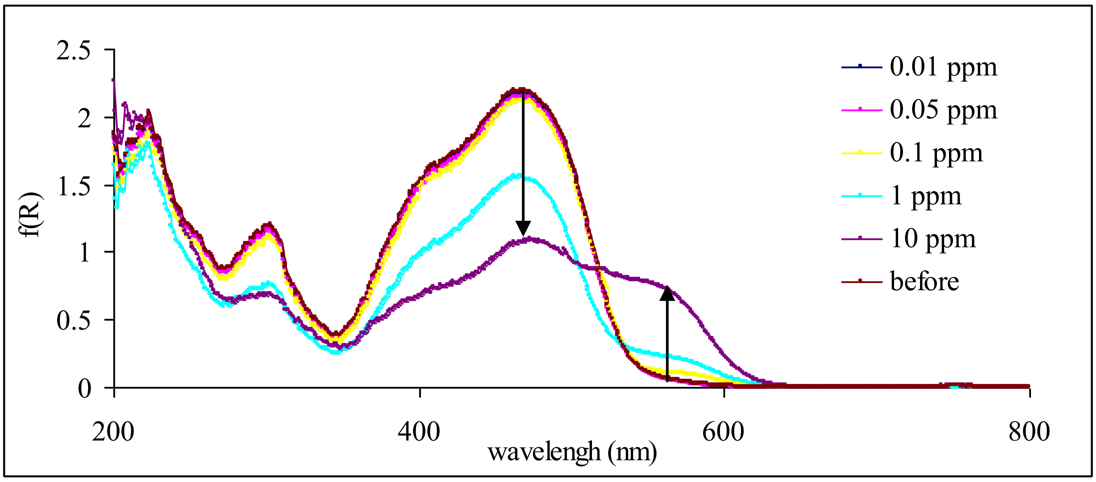


Fig. 4.12 The f(R) spectra of Si-PAN-Pb at different concentrations of Pb(II).

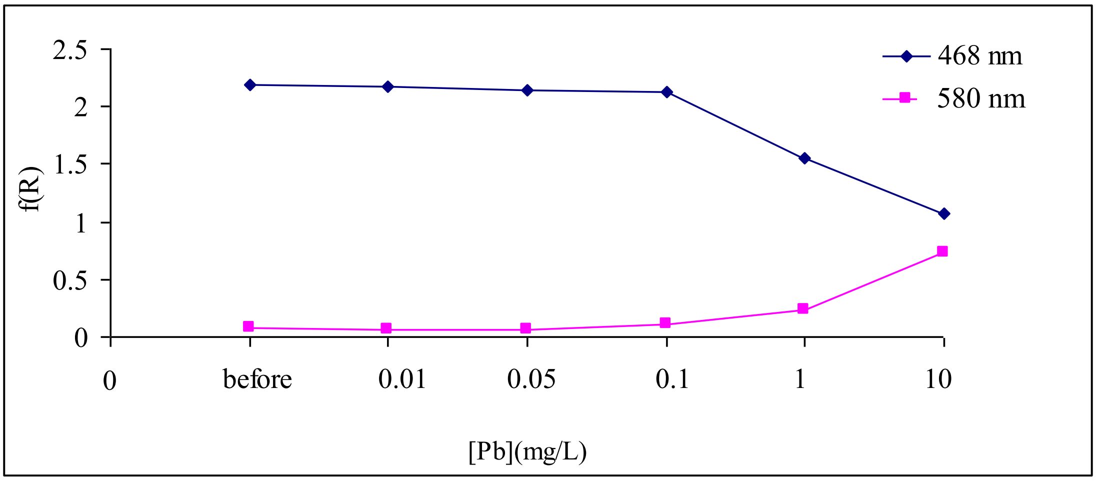


Fig. 4.13 The f(R) of Si-PAN-Pb at different concentrations of Pb(II) at 468 nm and 580 nm.

The change of f(R) of Si-PAN-Pb at different concentrations of Pb(II) was observed. The signal of Si-PAN-Pb at 468 nm decreased and the characteristic signal of Si-PAN-Pb at 580 nm increased with increase of concentration of Pb(II). The signal of Si-PAN-Pb at 580 nm was observed when the concentration of Pb(II) was 0.1 mg/L.

The percent colorimetric response (%CR) was calculated to determine the color change. The CR can be defined as follows: [69]

$$CR(\%) = \frac{(SP_0 - SP)}{SP_0} \times 100 \qquad (4.5)$$

$$\text{where: } SP = \frac{f(R)_{468nm}}{f(R)_{580nm} + f(R)_{468nm}} \qquad (4.6)$$

SP_0 is determined before exposure to any stimuli.

From the relation between f(R) and wavelength in Fig. 4.12, the percent colorimetric response was calculated and shown in Fig. 4.14.

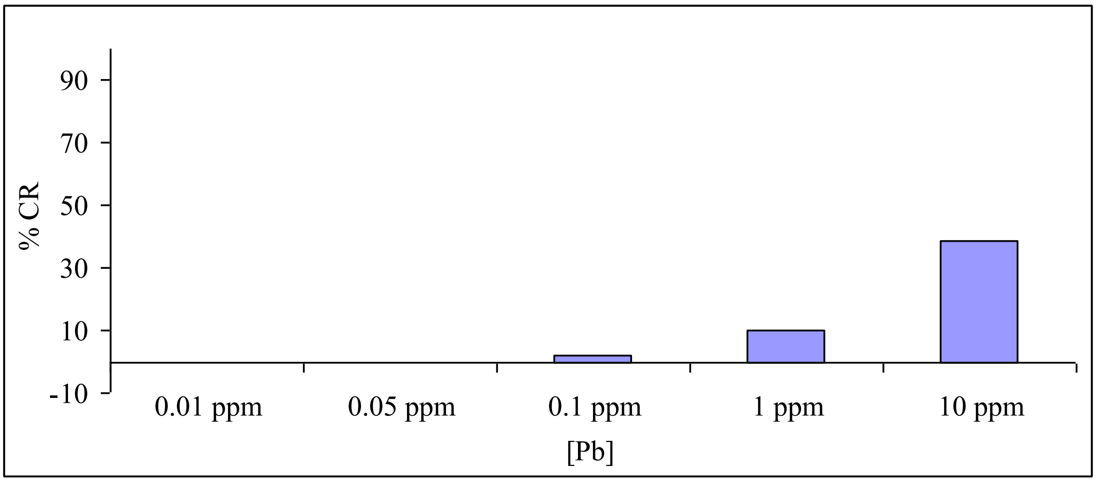


Fig. 4.14 Percent CR of Si-PAN-Pb at different concentrations of Pb (II).

The percent CR of Si-PAN-Pb increased with an increase of Pb(II) concentration. The color of Si-PAN-Pb was detected with naked-eye at 1 mg/L of Pb(II) with the percent CR of 10% but DR-UV-vis spectrometer can detect the absorption change at 0.1 mg/L.

According to the contamination of lead in drinking water that is in very low concentration level, while the lowest concentration of Pb(II) detected with Si-PAN

(5 mM) by naked-eye was 5 mg/L, the detection limit of this method was improved. The decrease of the concentration of PAN in coating step was carried out. In this work, the naked-eye detection limits of Si-PAN (0.1 mM) and Si-PAN (0.5 mM) were compared. Both of Si-PAN were used for extraction of Pb(II) in the concentration range of 0.005-10 mg/L under the optimum extraction conditions. The color of Si-PAN-Pb was investigated by 40 observers in comparison with the color of Si-PAN after stirring with Milli-Q water as a reference. The results are shown in Table 4.5.

Table 4.5 Number of observers detected the difference of color between Si-PAN and Si-PAN-Pb by naked-eye

Concentration of Pb(II) (mg/L)	**Number of observers**	
	Si-PAN (0.1 mM)	**Si-PAN (0.5 mM)**
< 0.05	7	3
0.05	0	0
0.1	7	2
0.5	8	5
1.0	17	18
5.0	0	8
10	0	0
> 10	1	4

(Conditions: 20 mg of Si-PAN, volume of solution = 5 mL, pH = 5, contact time = 10 min)

Most of observers indicated the color change of both Si-PAN (0.1 mM) and Si-PAN (0.5 mM) when the concentration of Pb(II) was 1 mg/L. This indicated that the naked-eye detection limit was not different between Si-PAN (0.1 mM) and Si-PAN (0.5 mM). Moreover, the color intensity of Si-PAN (0.1 mM) after extraction was less than that of Si-PAN (0.5 mM), therefore the observation of the color change of Si-PAN (0.1 mM) was more difficult. For the further studies, Si-PAN (0.5 mM) was used.

The naked-eye detection limit of Si-PAN (0.5 mM) was also investigated under the optimum extraction conditions in the concentration range of 0.1-2.0 mg/L of Pb(II) within one day (or intraday) to verify repeatability of this method and within three days (or interday) to verify that the method will provide the same results in different day. In case of intraday, the color of Si-PAN-Pb was investigated by 20 observers (2 times: morning and afternoon). In case of interday, the color of Si-PAN-Pb was investigated by 20 observers (one time per day for three days). The precision and the reproducibility of this method were determined by interday and intraday investigations, respectively. The results are shown in Table 4.6 and 4.7 for intraday and interday examinations, respectively.

Table 4.6 Number of observers detected the difference of color between Si-PAN and Si-PAN-Pb by naked-eye (intraday)

Concentration of Pb(II) (mg/L)	**Number of observers**	
	morning	**afternoon**
0.1	0	0
0.5	7	1
0.8	9	15
1.0	1	1
2.0	1	3
>2.0	2	0

(Conditions: 20 mg of Si-PAN, volume of solution = 5 mL, pH = 5, contact time = 10 min)

Table 4.7 Number of observers detected the difference of color between Si-PAN and Si-PAN-Pb by naked-eye (interday)

Concentration of Pb(II) (mg/L)	**Number of observers**		
	1st day	**2nd day**	**3rd day**
< 0.1	0	2	1
0.1	0	1	0
0.5	1	5	7
0.8	15	10	8
1.0	1	1	3
2.0	3	0	0
>2.0	0	1	1

(Conditions: 20 mg of Si-PAN, volume of solution = 5 mL, pH = 5, contact time = 10 min)

It was found that most of observers indicated the detection limit of Si-PAN (0.5 mM) at 0.8 mg/L of Pb(II). It was concluded that the Pb(II) naked-eye detection limit of 0.8 mg/L was obtained under the optimum extraction conditions as follows: Si-PAN (0.5 mM) = 20 mg, pH of Pb(II) solution = 5, volume of Pb(II) solution = 5.0 mL and contact time = 10 min.

4.4.2 Interfering ions

The effect of the interfering ions on Pb(II) extraction with Si-PAN was studied because from the preliminary test, some ions interfered the color change of Si-PAN. The alkaline and alkaline earth metals ions such as Na^+, K^+, Ca^{2+} and Mg^{2+} were studied because they usually present at high concentrations in the water. The percent extraction and the color of Si-PAN after the extraction step were investigated by varying concentrations of interfering ions. When the percent extraction significantly decreased (>10%), the interfering ion interferes the extraction of Pb(II). When the color of Si-PAN-Pb in the presence of the interfering ion changed from Si-PAN-Pb, this interfering ion interfere the naked-eye detection. The extraction of Pb(II) in the presence of Na^+, K^+, Ca^{2+} and Mg^{2+} are shown in Fig. 4.15

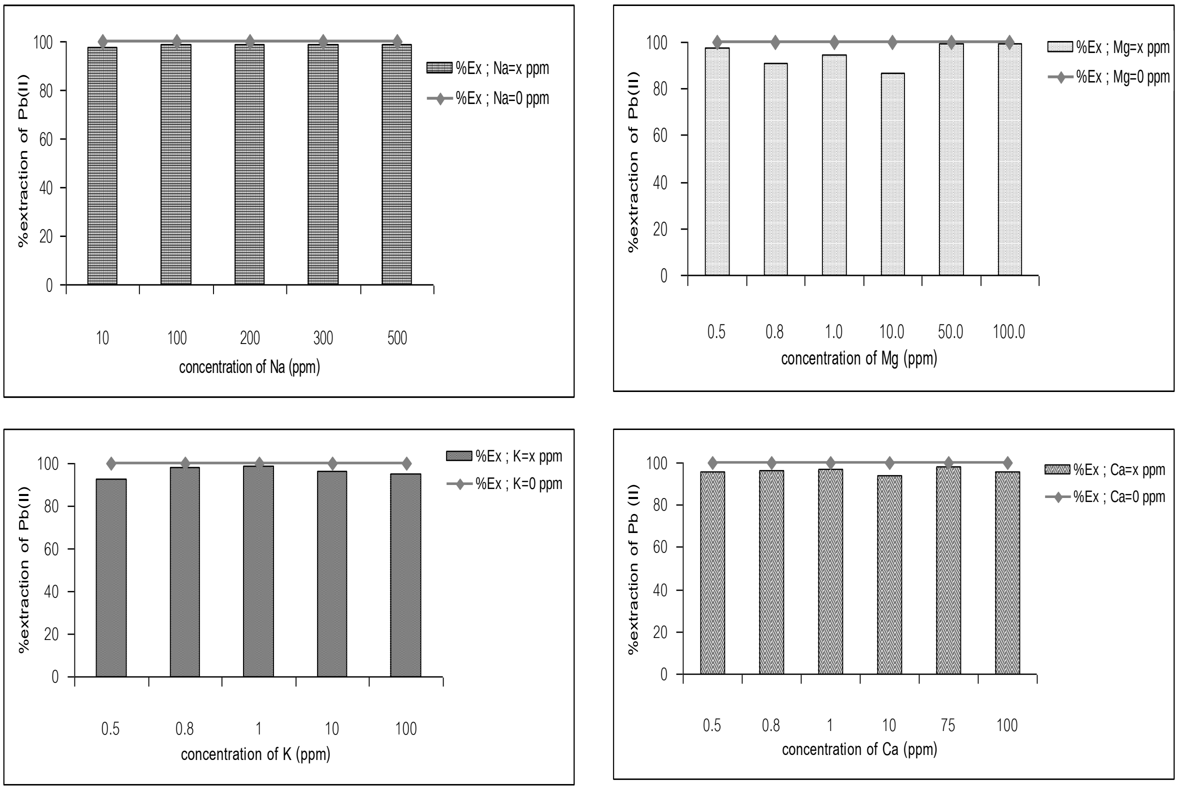


Fig 4.15 Percent extraction of Pb(II) in the presence of Na^+, K^+, Ca^{2+} and Mg^{2+}.

From the results, it was found that the percent extraction of Pb(II) was insignificantly different when the interfering ions were added in the range of 10-500 mg/L, 0.5-100 mg/L, 0.5-100 mg/L and 0.5-100 mg/L for Na^+, Mg^{2+}, K^+ and Ca^{2+}, respectively. This indicated that the preference of Si-PAN to Pb(II) was superior to Na^+, Mg^{2+}, K^+ and Ca^{2+}. Moreover, no color change of Si-PAN-Pb in the presence of Na^+, K^+, Ca^{2+} and Mg^{2+} was observed because PAN chelated only with transition metals but not for alkaline and alkaline earth.

In case of Ni(II), Zn(II), Cu(II), Fe(III), Mn(II), Cd(II), Co(II), and Ag(I), the extraction of 0.8 mg/L of Pb(II) in the presence of these metal ions at the concentration mentioned in Table 2.2 under the optimum conditions was carried out. The color of Si-PAN-Pb in the presence of Ni(II), Zn(II), Cu(II), Fe(III), Mn(II), Cd(II), Co(II), and Ag(I) was investigated. It was found that Cu(II), Fe(III) and Zn(II) affected to the color of Si-PAN-Pb because of high concentration of these metals (1.0 mg/L, 0.3 mg/L, and 5.0 mg/L for Cu(II), Fe(III) and Zn(II), respectively) whereas Cd(II), Cr(III), Mn(II) and Ag(I) did not interfere the color of Si-PAN-Pb at the concentration of 0.005 mg/L, 0.05 mg/L, 0.05 mg/L and 0.05 mg/L, respectively.

4.5 Shelf life of Si-PAN

For this work, the shelf life of Si-PAN was studied by keeping Si-PAN in a bottle and storing in a desiccator at room temperature. The shelf life of Si-PAN in a range of 1-12 weeks was considered in term of percent extraction of Pb(II) and the color of Si-PAN after extraction process. When the significant difference of percent extraction and the color change of Si-PAN after extraction were observed, Si-PAN was not able to be stored more than that period and it was not suitable for use. The percentages of extraction of Pb(II) within 12 weeks are shown in Fig 4.16.

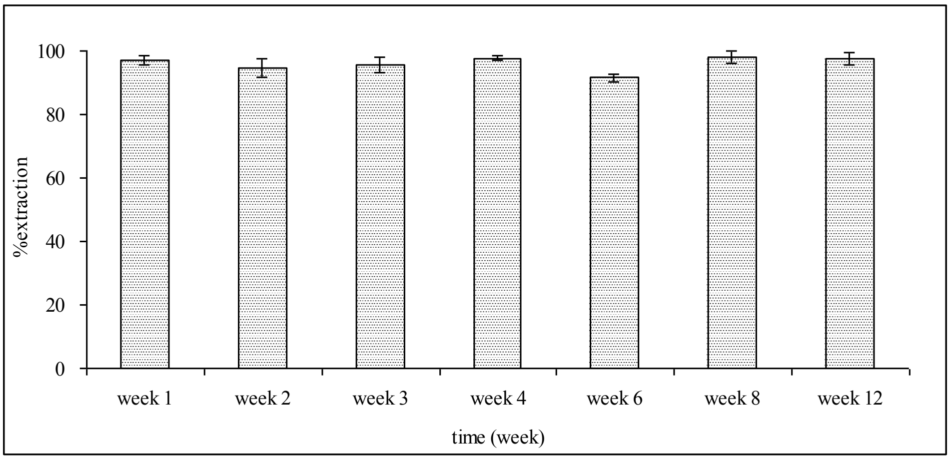


Fig 4.16 Percent extraction of Pb(II) for shelf life study.

The percent extraction of Pb(II) was higher than 90 during 1-12 weeks. The insignificant difference of percent extraction of Pb(II) was observed (calculated by student's pair t-test) and the Pb(II) naked-eye detection was still observed at 0.8 mg/L. This indicated that Si-PAN can be used as an efficiency naked-eye sensor or an efficient adsorbent for Pb(II) at least 12 weeks.

4.6 Determination of lead in real sample

The potential of Si-PAN as a sensor for determining Pb(II) in real water samples was studied under the optimum extraction conditions. In this work, 4 brands of drinking water were studied as real water samples. The effect of matrix in real water sample was examined with spiked method. The real water sample was spiked with Pb(II) standard solution to obtain the concentration of 0.8 mg/L. The concentration of Pb(II) in the solution was also determined by ICP-AES to confirm the concentration of Pb(II) in sample solution. The concentrations of Pb(II) determined by ICP-AES in sample solutions are shown in Table 4.8.

Table 4.8 Concentration of Pb(II) determined by ICP-AES in real water sample solutions with spiked and unspiked standard solution of Pb(II)

Sample	**Concentration of Pb(II) (mg/L)**		**%Recovery**
	unspiked	**spiked**	
Sample 1	nd	0.824	103
Sample 2	nd	0.871	109
Sample 3	nd	0.836	105
Sample 4	nd	0.826	103

The colors of Si-PAN-Pb of the real water sample spiked and unspiked with standard solution of Pb(II) were compared. The color of Si-PAN-Pb of the unspiked real water sample was not different from Si-PAN-MilliQ but the color of Si-PAN-Pb of the spiked real water sample was different from Si-PAN-MilliQ. The colors of Si-PAN-Pb of real water sample and Si-PAN-Pb of spiked real water sample were compared. It was found that the color of Si-PAN-Pb of unspiked real water sample differed from that of spiked real water sample. It indicated that Si-PAN (0.5 mM) can use as a solid sensor for Pb(II) in drinking water containing the concentration of Pb(II) at least 0.8 mg/L. But the acceptable concentration of lead in drinking water was 0.05 mg/L. Therefore, Si-PAN (0.5 mM) can use as only screening solid sensor for Pb(II) at the concentration of 0.8 mg/L.

CHAPTER V

CONCLUTION

A simple method for Pb(II) naked-eye detection in drinking water was developed by using silica gel coated with a suitable ligand as a solid sensor. Three types of ligand coated onto silica gel were dithizone, purpurin and 1-(2-pyridylazo)-2-napthol (PAN). The preliminary results showed that silica gel coated with PAN (Si-PAN) provided high extraction efficiency of Pb(II) which was considered in term of percent extraction and it was a good naked-eye detector for various metal ions. Therefore, Si-PAN was used as a naked-eye sensor for Pb(II). The optimum conditions for preparation of Si-PAN were summarized as follows: stirring time = 1 hr, amount of silica gel = 2 g and concentration of PAN (in ethanol) for coating PAN onto silica gel = 5 mM. Si-PAN was characterized by DR-UV-vis spectrophotometry. The maximum absorption wavelength of Si-PAN was observed at around 468 nm while the absorption band of silica gel was not found at the same wavelength. The maximum wavelength of Si-PAN was in the similar range of the maximum wavelength (400-500 nm) of several azo compounds

The extraction of 5 mg/L Pb(II) solution by Si-PAN coated with 5 mM PAN solution in batch experiment was studied as the functions of pH and contact time. The results showed that Si-PAN was able to extract Pb(II) from aqueous solutions at pH 4.5-5.5 with 90% extraction within 10 min. After Pb(II) extraction, it was found that the color of Si-PAN obviously differed from Si-PAN. The color of Si-PAN changed from orange to pink. Then, the lowest concentration of Pb(II) in the solution which was able to be observed the color change by naked-eye was studied. The results showed that the concentration of PAN which was able to be detected the lowest concentration of Pb(II) was 0.5 mM and the lowest concentration of Pb(II) was 0.8 mg/L.

Si-PAN showed high selectivity towards Pb(II) in comparison with Na^+, K^+, Mg^{2+} and Ca^{2+}. No color change of Si-PAN in the presence of alkali and alkaline earth was observed while Cu(II), Fe(III) and Zn(II) affected to the color of Si-PAN after extraction. Moreover, it was found that Si-PAN was used as an efficiency quantitatively naked-eye sensor for Pb(II) at least 12 weeks. The determination of Pb(II) in drinking water by naked-eye detection using Si-PAN coated with 0.5 mM PAN solution under the optimum extraction conditions in comparison with ICP-AES method was achieved .

Suggestions for future work

As the result and discussion, Si-PAN (0.5 mM) can use as a solid sensor for 0.8 mg/L of Pb(II) in aqueous solution. The naked-eye detection limit of Pb(II) is still higher than the maximum acceptable concentration (mg/L). Moreover, the bonding of PAN and silica gel was not chemical bond resulting in destroy by magnetically stirring. The decrease of PAN on silica gel affected to the efficiency of extraction of Pb(II). To improve the naked-eye detection of Pb(II), the chemical bonding of PAN and silica gel was interesting.

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VITA

Miss Rungnapa Kongsung was born on May 6, 1986 in Nakornpathom, Thailand. She received her Bachelor degree of Science in Chemistry from Chulalongkorn University in 2009. She has been graduated student at the Department of Chemistry Chulalongkorn University and become a member of Environmental Analysis Research Unit under supervisions of Assistant Professor Dr. Wanlapa Aeungmaitrepirom. She finished her postgraduate study in the leading of the Master's degree of Science in 2010.